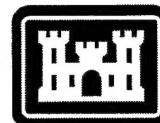


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A Review of the Thermodynamics of Frost Heave

Karen S. Henry

September 2000

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Technical Report
ERDC/CRREL TR-00-16



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of Engineers®**
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A Review of the Thermodynamics of Frost Heave

Karen S. Henry

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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS

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Abstract: Thermodynamic equilibrium requires a balance of thermal, mechanical, and chemical forces. The general equation for mechanical equilibrium between two phases describes capillary effects in porous materials, important in both unsaturated water flow and in understanding ice/water interfaces in freezing soil. The Gibbs-Duhem equation, which relates changes in chemical potential of a substance to changes in temperature, pressure, and presence of other chemicals, is of critical importance in understanding the flow of water in freezing soils. Osmotic pressure, related to the chemical potential of the substance, is useful in formulating expressions for total soil water pressure because soil water contains solutes, and the influence of soil particle surfaces can be "approximated" as solutes. It is the gradient in the total soil water pressure that drives flow to the freezing front in soils. The generalized Clapeyron equation, based on the thermodynamic equilibrium of ice and water in soils (e.g., Loch 1978), is utilized by the thermo-

dynamically based models of Miller (1978) and Gilpin (1980). In these models Fourier's Law and Darcy's Law describe heat and mass transfer in the frozen fringe, respectively, and mass flow and heat flow are coupled by one equation that describes heat transfer in the frozen soil. Ice lenses start to grow when the effective stress in the frozen fringe becomes zero (Miller 1978, Gilpin 1980). Once an ice lens is established, liquid water is removed from the adjacent pores because of phase change, and water flows up through the soil to replenish the liquid water. If the rate of water loss caused by phase change is matched by the rate of water flow to replenish the liquid water, the ice lens will continue to grow in thickness. If the hydraulic conductivity of the soil limits the rate of water replenishment to the ice lens for the given rate of heat loss, soil water will freeze at increasing depths with associated changes in the depth and thickness of the frozen fringe.

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PREFACE

This report was prepared by Dr. Karen S. Henry, Research Civil Engineer, Civil Engineering Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Engineer Research and Development Center (ERDC), Hanover, New Hampshire.

This report was originally prepared as a paper for Geology 600 for Dr. Bernard Hallet, Professor of Glacial and Periglacial Geomorphology, Department of Geological Sciences, University of Washington, Seattle, while the author was on Department-of-the-Army-sponsored long-term training. Final publication was funded by U.S. Army Corps of Engineers work unit AT24-SP-006, *Thermodynamics of Frost Heave*.

While taking Professor Hallet's Geology 600 course, the need for introductory material on this topic became evident. Therefore, this report is intended to be used as a primer on the thermodynamics of frost heave in soils for those who are beginning to study this interesting phenomenon.

The author thanks Dr. Bernard Hallet, Professor of Glacial and Periglacial Geomorphology, Department of Geological Sciences, University of Washington, Seattle, and Dr. Patrick Black of CRREL for technically reviewing this report. Dr. Samuel Colbeck also provided technical review and encouragement to publish this work.

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A Review of the Thermodynamics of Frost Heave

KAREN S. HENRY

INTRODUCTION

During frost heaving of soil when the soil is freezing from the top down, water in the soil pores flows upward to the freezing front because of a gradient in the soil moisture pressure (or tension). This occurs even when the soil pores are not saturated. Ice lenses form and grow at or slightly above the freezing front and cause great uplifting forces. Understanding this process is not intuitive. However, thermodynamics, or the study of heat and work and the conversion of one of these energy forms to the other, provides a means of understanding frost heave. This report was written to make thermodynamic concepts accessible and to provide the background needed to help engineers and scientists understand two aspects of soil freezing: the flow of water to the freezing front, and the initiation of ice lenses that cause the soil to heave. It is a review and summary of 1) the thermodynamic principles that are important in modeling frost heave in soils, and 2) past research using equilibrium thermodynamics that has contributed to the understanding of frost heaving. The intent is for most readers to use this report without reference to texts. For a more complete study of thermodynamics, Castellan (1983) is highly recommended. Some difficult concepts are also illuminated very well by Silver and Nydahl (1977).

The sections "Thermodynamic fundamentals" and "Thermodynamic equilibrium" present material from university senior-level physical chemistry, with a special emphasis on topics relevant to freezing soils. Thermodynamic definitions, concepts, and fundamental equations are provided in "Thermodynamic fundamentals." "Thermodynamic equilibrium" presents thermodynamic equilibrium conditions and conditions under which thermodynamic processes such as phase change will spontaneously occur. "Thermodynamic equilibri-

um" also includes definitions of thermal, mechanical, and chemical equilibrium, and the relationships among forces acting on systems in equilibrium are also examined. Significant contributions to the understanding of frost heave, based on equilibrium thermodynamics, are reviewed in "Thermodynamic treatment of frost heave." This section begins with early work that led to the development of thermodynamic relations between water and ice in soil, followed by a brief presentation of the significant aspects of two models of frost heaving. "Summary of current understanding of frost heave" summarizes our current understanding of frost heave without the use of equations.

This report is an introduction to the thermodynamics of frost heave, and is not a comprehensive review of all recent work on the subject or on frost heave modeling. Nonetheless, two areas of significant development are mentioned below for those readers who want to pursue this topic in depth. This report will provide some of the background required for further study of the material discussed below.

First, considerable progress has been made toward understanding the nature of the unfrozen water that persists in soils at temperatures below the freezing temperature of bulk water (e.g., Dash et al. 1995, Wettlaufer 1998). The focus of the work by Dash et al. (1995) and Wettlaufer (1998) is on isolating the roles that curvature, confinement in pores, physical characteristics of ice surfaces, and the presence of impurities in soil water play on the thickness and mobility of unfrozen water in freezing soils.

Second, regarding the ability to predict the deformation of soils in response to freezing or thawing, engineers have had great success in predicting material behavior by treating it as a continuum. Blanchard and

Fremond (1985) published a model of soil frost heaving and thaw settlement that utilized the continuum approach. The constitutive laws used to describe the soil behavior were elastic for the unfrozen soil and viscoplastic when frozen. Michalowski (1992, 1993) extended that work to account for more factors affecting frost heave (e.g., three-dimensional stress state of the soil). He used constitutive relations to describe the rate of deformation of the soil during frost heave, as well as the constitutive relations of heat conduction (Fourier's Law), water flow (Darcy's Law), and a constitutive law describing the relation between stress and strain in the frozen soil or soil skeleton. Recently, Hartikainen and Mikkola (1997) reported progress on using equilibrium thermodynamics to predict the movement and phase change of water in freezing soil along with constitutive models to predict the deformation of the soil due to frost heave.

THERMODYNAMIC FUNDAMENTALS

Definitions, first, and second laws

A **thermodynamic system** is a portion of the universe set aside for study. There are three types: open, closed, and isolated. An open system can exchange energy and mass with its surroundings. The open system is thus specified by space rather than the matter contained within the space, and the volume occupied by an open system is a control volume. In freezing soil, a volume through which water, heat, and soil flow is an open system. A closed system can exchange only energy with its surroundings and is modeled with a control mass; a mass of soil through which heat but no matter flows is a closed system. An isolated system can exchange neither energy nor mass with its surroundings.

A **property** is a system characteristic that can be measured or determined from other measurements. The state of a system is defined when all of its properties are specified. Properties are classified as either extensive or intensive. Extensive properties are additive, meaning that the value of the property is obtained by summing the values of the property in every part of the system. These include mass, volume, length, area, and number of moles of a species in a system. Intensive properties do not depend on system size. These include pressure, temperature, specific volume, stress, surface tension, and force per unit length.

A **change in the state of a system** results from processes such as energy or mass flow across its boundaries or internal processes that cause its properties to change. A **process** is a series of events causing a change of state, and a **path** is the sequence of states that the system assumes between initial and final states. There are many different types of processes, or stages in pro-

cesses, including adiabatic (no heat transfer between system and surroundings), isothermal, isobaric, or isochoric (constant volume).

Equilibrium is defined as a state of rest—i.e., the system properties do not change with time. Thermodynamic equilibrium is an equilibrium state where there is a balance of thermal, mechanical, and chemical forces. If a system always deviates from equilibrium only infinitesimally during a process, then the process is reversible. Real processes are always irreversible, but reversible processes are studied to determine maximum or minimum amounts of work that can be produced by them.

Heat flows across a system boundary in response to a temperature gradient. Heat is path-dependent, meaning that the amount of heat flow that occurs depends on the process itself. Heat appears only at the boundary of a system during a change in state. It is manifested by temperature change in the surroundings.

Work is energy that flows across the boundary of a system during a change in state that is completely convertible to lifting a weight in its surroundings. Like heat, work is path-dependent, appearing only at the boundary of a system during a change in state, and is manifested by an effect in the surroundings (e.g., the lifting of a weight). It occurs as a result of a potential gradient other than temperature (e.g., a pressure gradient). The equation for mechanical work is $\delta W = Fdl$, where F refers to a "generalized force," and l refers to a "generalized displacement." (The symbol δ indicates path dependence and d , path independence.) If the force is independent of direction and the rate of change of the process (i.e., it is path-independent), then the work mode is reversible (that is, the amount of energy added in a forward process is equal to the amount of energy removed in a reverse process).

All intensive thermodynamic properties are generalized forces, and all extensive properties are generalized displacements—including length, volume, area, mass, and number of moles of a substance. Reversible work is an idealization of real processes—examples are frictionless pulleys or resistanceless wires. Types of reversible work are defined in Table 1. For nonreversible work, relationships other than those given in Table 1 must be used to account for the energy that is not converted to work.

Entropy is the extensive property of a system associated with heat energy, and temperature is the intensive property. Heat can be expressed as $\delta Q_{\text{rev}} = TdS$, where S is the entropy. Entropy is a measure of the decrease in the system's ability to do work. It can be associated with mass entering or leaving a system, or both, and can be exchanged across system boundaries because of heat transfer.

Table 1. Types of reversible work done by thermodynamic systems (Silver and Nydahl 1977).

Type of work	Generalized force	Generalized displacement	Element of work
Volumetric	P	$-V$	PdV
Length	F	l	$-Fdl$
Surface	ψ (surface tension)	A_r (area)	$-\psi dA_r$
Gravitational	gz	m (mass)	$-gzdm$
Centrifugal	$-r^2\omega^2/2$	m (mass)	$\frac{r^2\omega^2}{2}dm$
Electrical	ϵ	q	$-\epsilon dq$
Chemical*	μ	η	$-\mu d\eta$

* μ = chemical potential (see eq 18); η = number of moles.

Heat capacity, C , is the amount of heat, δQ , that must be added to a system to change the temperature by dT , or $C = \delta Q/dT$. C_v is the heat capacity at constant volume, and C_p is the heat capacity at constant pressure.

The fundamental thermodynamic principles needed for the study of freezing soils are

The zeroth: If two systems are in thermal equilibrium with a third, then they are in equilibrium with each other.

Conservation of mass: Matter is not created or destroyed; it can only be changed to other chemical species or to energy.

First law: Energy is conserved. A mathematical statement of the first law is

$$dU = \delta Q - \delta W, \text{ or } \Delta U = Q - W \quad (1)$$

where U is the energy of the system.

Second law: Every system that is left to itself will change toward a condition in which its ability to do work will have decreased. Another way to express the second law is that entropy can be produced, but never destroyed. A mathematical statement of the second law is

$$\int dS > \oint \frac{\delta Q}{T}, \text{ or } dS > \frac{\delta Q}{T}. \quad (2a)$$

For all irreversible cycles

$$\oint \frac{\delta Q}{T} < 0 \quad (2b)$$

and for any change of state in an isolated system

$$dS > 0. \quad (2c)$$

Other important definitions include the composite functions, so called because they are combinations of

other functions (properties) of a state. The composite functions are Gibbs free energy, enthalpy, and Helmholtz free energy. They were defined for convenience from applying the first and second laws to systems under various constraints. For example, Gibbs free energy (a quantity of great interest in studying freezing soils) was developed to help study systems that exist at constant temperature and pressure.

Gibbs free energy, G : For constant temperature and pressure, $d(PV) = PdV$ and $d(TS) = TdS$. Applying the first law in the form $\delta Q = dU + \delta W$ and the relation that $TdS \geq \delta Q^*$ (from eq 2a), we obtain $TdS \geq dU + \delta W$, where $\delta W = PdV + \delta W_a$ and W_a is all of the work other than PV work. Thus, $-d(U + PV - TS) \geq \delta W_a$, and $G \equiv U + PV - TS$ becomes a convenient definition. Thus, at equilibrium $\partial G/\partial W_a = 0$; and, $\partial G/\partial W_a < 0$ for a spontaneous transformation to occur at constant temperature and pressure. This will be discussed again in the section "Thermodynamic equilibrium."

Enthalpy, H : $H \equiv U + PV \equiv G + TS$. Enthalpy applies to systems at constant pressure, such as laboratory systems at atmospheric pressure. It was developed similarly to Gibbs free energy by applying the first law at constant pressure.

Helmholtz free energy, A : $A \equiv U - TS \equiv G - PV$. Helmholtz free energy was developed for constant temperature systems.

Fundamental equations

The basic balance equations of thermodynamics relate the heat and work transferred during a process to a difference in thermodynamic functions such as enthalpy and entropy. For a closed system, the energy balance equation is eq 1. Making substitutions for the heat term (see the definition of entropy) and for the work term (from Table 1) yields

$$dU = TdS - PdV + Fdl + \psi dA_r + \epsilon dq + \sum \mu_i d\eta_i + gzdm + \left(r^2 \frac{\omega^2}{2} \right) dm +, \text{ etc. } \dots \quad (3a)$$

Equation 3a is known as the property relationship (Silver and Nydahl 1977). For the engineering study of thermodynamics, this relationship is often stated for systems in which there is only expansive work:

$$dU = TdS - PdV. \quad (3b)$$

However, for the study of freezing soil, the property relationship often used is

$$dU = TdS - PdV + \sum \mu_i d\eta_i. \quad (3c)$$

* In a reversible process, $dS = \frac{\delta Q}{T}$.

For eq 3b and c, respectively, using the definitions of Gibbs free energy, enthalpy, and Helmholtz free energy, differentiating and substituting eq 3b or 3c for dU results in

$$dG = -SdT + VdP \quad (4a)$$

or

$$dG = -SdT + VdP + \sum_i \mu_i d\eta_i \quad (4b)$$

$$dH = TdS + VdP \quad (5a)$$

or

$$dH = -TdS + VdP + \sum_i \mu_i d\eta_i \quad (5b)$$

$$dA = -SdT - PdV \quad (6a)$$

or

$$dA = -SdT - PdV + \sum_i \mu_i d\eta_i \quad (6b)$$

Equations 3 through 6 are known as the four fundamental equations of thermodynamics.

THERMODYNAMIC EQUILIBRIUM

Equilibrium thermodynamic relations are often used in soil freezing and frost heave models (analytical and numerical); therefore, their derivations are now presented. For a system undergoing cyclical changes in state, the process is reversible if, at the end of each cycle, the surroundings are restored to their original state. At every stage of this process, the system departs from equilibrium only infinitesimally. Thus, the condition for reversibility is an equilibrium condition (e.g., Castellan 1983):

$$TdS = \delta Q_{rev} \quad (7a)$$

and for irreversible (natural) processes

$$TdS > \delta Q_{rev} \quad (7b)$$

The composite functions are used to describe equilibrium and spontaneous transformation conditions of systems under the constraints for which they were defined. For example, at constant temperature, $d(TS) = TdS$, and applying eq 7 ($TdS \geq \delta Q$) together with the first law and the substitution that $\delta Q = TdS = d(TS)$ results in

$$-dU + d(TS) \geq \delta W \quad (8)$$

$$-d(U - TS) \geq \delta W \quad (9)$$

$$\text{or} \quad -dA \geq \delta W \quad (10)$$

In the absence of work, the isothermal equilibrium condition is $dA = 0$; furthermore, a spontaneous process produces negative Helmholtz free energy. In other words, a constant temperature system minimizes Helmholtz free energy.

A similar derivation can be done for constant pressure and temperature processes to show that the spontaneity condition is

$$-dG \geq \delta W \quad (11)$$

Thus, at constant temperature and pressure and in the absence of work, the equilibrium condition is $dG = 0$; and, a spontaneous process produces negative Gibbs free energy.

Thermal equilibrium

Substituting $TdS \geq \delta Q$ into the first law results in

$$-dU - \delta W + TdS \geq 0 \quad (12)$$

For an isolated system, $dU = \delta W = \delta Q = 0$; thus, eq 12 applied to an isolated system is

$$dS \geq 0 \quad (13)$$

Since $dS = (\delta Q_{rev} / T)$, if a positive quantity of heat passes from region a to b within an isolated system, then

$$dS = dS_a + dS_b = \left(\frac{1}{T_b} - \frac{1}{T_a} \right) \delta Q_{rev} \quad (14)$$

and for a spontaneous process, $dS > 0$; therefore, $T_a > T_b$. At equilibrium, $dS = 0$ and $T_a = T_b$. Thus, a system in thermal equilibrium has the same temperature in all regions, and when it is not in equilibrium, heat flows from regions of high temperature to low temperature.

Mechanical equilibrium

For a constant-volume, constant-temperature system divided into regions a and b , if region a expands reversibly by dV_a then region b contracts by $dV_b = -dV_a$. According to eq 6a, $(\partial A / \partial V)_T = -P$, or $dA = -PdV$, and $dA = dA_a + dA_b$. Therefore, $dA = (P_b - P_a) dV_a$. Since $\delta W = 0$ (for a constant volume), from eq 10 and the second law, $dA \leq 0$ and, therefore, $P_a \geq P_b$. In other words, for a spontaneous expansion of region a into b , the pressure must be greater in a . At equilibrium, $P_a = P_b$. This is a lot of work to get an obvious result, but this type of analysis is helpful when less intuitive processes are described as below.

For a constant-volume, constant-entropy system consisting of two phases a and b with an interface, ψ ,

between them (e.g., ice and water), the total energy is the sum of the energy of the various parts:

$$dU = dU_a + dU_b + dU_\Psi. \quad (15)$$

The surface work term (see Table 1) is ΨdA_r ; therefore,

$$dU = -P_a dV_a - P_b dV_b + \Psi dA_r. \quad (16)$$

At equilibrium, $dU = 0$, therefore

$$(P_a - P_b)dV_a = \Psi dA_r. \quad (17)$$

Thus, at equilibrium there is a pressure difference across the interface unless it is planar. If the interface is planar, $dA_r = 0$ and $P_a = P_b$. The difference in pressure across a curve interface is the physical reason for capillary rise and depression of liquids in porous materials (e.g., Castellan 1983).

Chemical equilibrium

Conditions for chemical equilibrium

From eq 4b,

$$\left(\frac{\partial G}{\partial \eta_i} \right)_{T,P,\eta_{j \neq i}} = \mu_i. \quad (18)$$

The chemical potential of a substance, μ_i , is the Gibbs free energy increase per mole of substance i added to a system at constant temperature, pressure, and numbers of moles of other substances (j) present in the system. For a system consisting of a pure substance i , $dG = -SdT + VdP$ (eq 4a), and this can be divided by η_i so that

$$d\mu_i = -\bar{S}dT + \bar{V}dP \quad (19)$$

where \bar{S} and \bar{V} are the entropy and volume per mole of substance i , respectively.

For a system at constant temperature, pressure, and numbers of moles, j , and divided into two regions, a and b :

$$dG = dG_a + dG_b = \mu_{ia}d\eta_i + \mu_{ib}d\eta_i. \quad (20)$$

If $d\eta_i$ moles go into b , and $d\eta_i$ moles leave a , then $dG_a = \mu_{ia}(-d\eta_i)$; $dG_b = \mu_{ib}d\eta_i$ and $dG = (\mu_{ib} - \mu_{ia})d\eta_i$.

A spontaneous reaction requires that dG be negative, therefore $\mu_{ib} < \mu_{ia}$, and matter flows from regions of high chemical potential to low chemical potential. At equilibrium, $dG = 0$ and $\mu_{ib} = \mu_{ia}$. Thus, chemical potentials for substance i must have the same values throughout a system in chemical equilibrium.

Properties of chemical potential

Equation 18 shows that the chemical potential of a component is a function of temperature, pressure, and amounts of other chemical species. This leads to interesting system behavior. If two regions in the same system are at different pressures or temperatures, with all other properties being held constant, then they will have different chemical potentials. At constant temperature and pressure, the chemical potential of a component in two regions may be different due to different concentrations of it. Another property of chemical potential is that, at constant concentration of a species, a pressure difference and a temperature difference may compensate each other, thereby maintaining a constant chemical potential.

Other properties of chemical potential can be deduced. At constant temperature for a single-component system, the pressure dependence derived from eq 4a is $dG = VdP$, which can be integrated to obtain

$$G = G^o(T) + \int_{P^o}^P VdP \quad (21)$$

where G^o is the Gibbs free energy at one atmosphere of pressure, P^o . For liquids and solids (constant volume), this relation becomes

$$G = G^o(T) + V(P - P^o). \quad (22)$$

For ideal gases

$$V = \frac{nRT}{P}$$

and

$$G = G^o(T) + nRT \ln \left(\frac{P}{P^o} \right) \quad (23)$$

or

$$\mu = \mu^o(T) + RT \ln \left(\frac{P}{P^o} \right) \quad (24)$$

where μ^o is the chemical potential of a pure substance at one atmosphere. For solid, liquid, or gaseous mixtures of ideal solutions (i.e., $P_i = x_i P_i^o$, where x_i is the mole fraction of the substance and P_i is its partial pressure)

$$\mu_i = \mu_i^o(T, P) + RT \ln x_i. \quad (25)$$

The dependence of Gibbs free energy on temperature at constant pressure can be expressed by using eq 4a, which yields

$$\left(\frac{\partial G}{\partial T} \right)_P = -S. \quad (26)$$

The dependence of G/T on temperature at constant pressure is also of interest, and it is derived by applying the ordinary rule of differentiation to $\partial(G/T)/\partial T$, eq 26, and using the definition of enthalpy, H , to obtain (e.g., Castellan 1983)

$$\left(\frac{\partial \frac{G}{T}}{\partial T}\right) = \frac{-H}{T^2}. \quad (27)$$

Equation 27 is known as the Gibbs–Helmholtz equation.

For an equilibrium mixture (i.e., μ_i is constant) at constant temperature and pressure,

$$dG = \sum_i \mu_i (d\eta_i) \quad (28)$$

which can be integrated to obtain

$$\Delta G = \sum_i \mu_i (\Delta \eta_i) \quad (29)$$

For $\eta_{\text{initial}} = 0 = G_{\text{initial}}$, we obtain

$$G = \sum_i \eta_i \mu_i. \quad (30)$$

Differentiating eq 23 and setting it equal to eq 4b results in

$$\sum_i \eta_i d\mu_i = -SdT + VdP. \quad (31)$$

Equation 31 is the Gibbs–Duhem equation. Note that for constant temperature and pressure,

$$\sum_i \eta_i d\mu_i = 0. \quad (32)$$

Chemical equilibrium between phases of a single component

For a system in chemical equilibrium containing more than one phase of a substance, the chemical potentials of the substance in all phases must be equal. For a system containing a pure substance only, we know from eq 19 that

$$\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}. \quad (33)$$

Thus, a plot of μ vs. T for any phase will have a slope of $-\bar{S}$ and equilibrium between phases occurs when the chemical potentials of both phases are equal (Fig. 1). Proceeding from solid to liquid to vapor, the negative slopes increase, reflecting the increase in entropy (eq 33). Figure 1 shows that if the chemical potential of the liquid phase is lowered (e.g., adding salt to water lowers the chemical potential of the water—see eq 25), there will be an accompanying decrease in the freezing point and increase in the boiling point. From eq 19

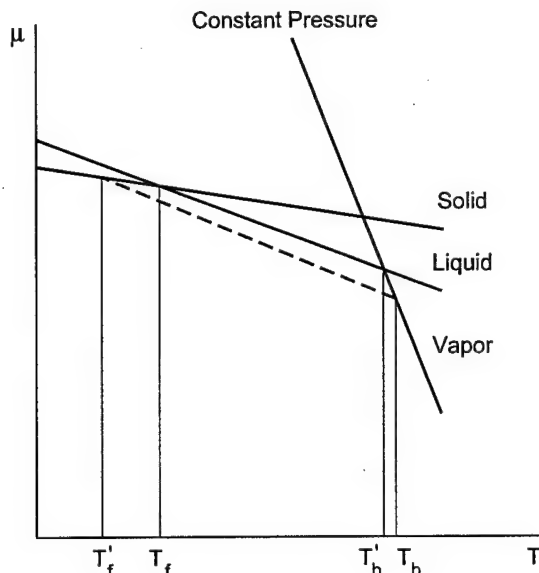


Figure 1. Plot of μ as a function of temperature for a pure solvent (solid lines). The dashed line represents the chemical potential of the liquid solvent when solute i is present. (After Castellan 1983.)

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}. \quad (34)$$

Consider the equilibrium of a pure substance in two phases, a and b :

$$\mu_a(T, P) = \mu_b(T, P). \quad (35)$$

From eq 34 we know that a pressure increase, dP , will result in a chemical potential increase, $d\mu$. This will be accompanied by a change in equilibrium temperature (e.g., Fig. 1). At $(T + dT, P + dP)$, the new equilibrium condition can be expressed as

$$\mu_a(T, P) + d\mu_a = \mu_b(T, P) + d\mu_b. \quad (36)$$

Subtracting eq 36 from 35 results in $d\mu_a = d\mu_b$, or by substituting each of these expressions into eq 19 and setting these equal to each other,

$$(\bar{S}_b - \bar{S}_a)dT = (\bar{V}_b - \bar{V}_a)dP \quad (37)$$

or

$$\left(\frac{\partial P}{\partial T}\right) = \left(\frac{\Delta S}{\Delta V}\right). \quad (38)$$

Equation 38 is known as the Clapeyron equation, an important equation of equilibrium between two phases of a substance. Phase diagrams, such as the one for pure water shown in Figure 2, consist of lines that represent

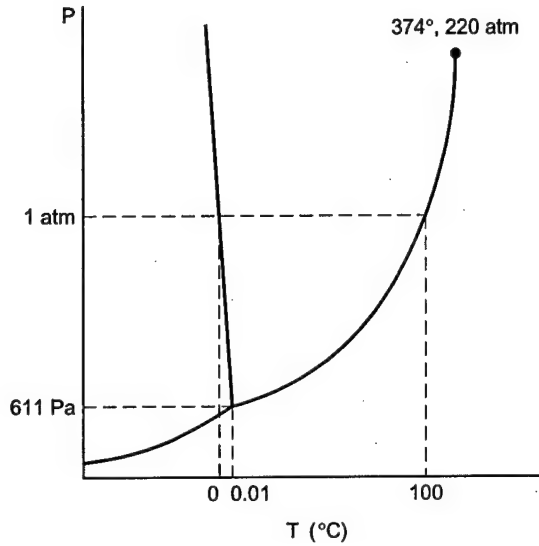


Figure 2. Phase diagram for water.

the pressure and temperature conditions for phases in equilibrium.

Osmotic pressure

Osmotic pressure, Π , is the pressure required to maintain equilibrium between a solution and the pure solvent across a semi-permeable membrane through which the solvent, but not the solute, can diffuse. The osmotic pressure is easily determined using the chemical potential requirement of equilibrium. For the solvent on both sides of the membrane,

$$\mu(T, P + \Pi, x) = \mu^o(T, P). \quad (39)$$

From eq 25 we know that $\mu(T, P + \Pi, x) = \mu^o(T, P + \Pi) + RT \ln x$. Substituting this into eq 39 results in

$$\mu^o(T, P + \Pi) + RT \ln x = \mu^o(T, P). \quad (40)$$

Using eq 34, $d\mu^o = \bar{V}^o dP$ and integrating from P to $P + \Pi$, we get

$$\mu^o(T, P + \Pi) - \mu^o(T, P) = \int_P^{P+\Pi} \bar{V}^o dP. \quad (41)$$

Substituting eq 41 into 40 yields

$$\int_P^{P+\Pi} \bar{V}^o dP + RT \ln x = 0. \quad (42)$$

For an incompressible solvent in an ideal solution the molar volume remains constant, and

$$\Pi = \frac{-RT \ln x}{\bar{V}^o}. \quad (43)$$

If the solution is dilute, then $\ln x = \ln(1 - x_2) = -x_2$, where x_2 is the mole fraction of the solute, and because $n_2 \ll n$,

$$-x_2 \approx -\frac{n_2}{n} \quad (44)$$

where n refers to the number of moles. Thus, substituting eq 44 into eq 43 yields

$$\Pi = \frac{n_2 RT}{n \bar{V}^o} \quad (45)$$

but $V \approx n \bar{V}^o$, so

$$\Pi = \tilde{c} RT \quad (46)$$

where \tilde{c} is the solute concentration (mol m^{-3}). The concept of osmotic pressure is useful in formulating expressions for total soil water pressure because soil water contains solutes. Furthermore, the influence of soil particle surfaces on the chemical potential of the soil water can be "approximated" as solutes.

Summary

Fundamental thermodynamic principles have been reviewed in the above sections. The relations and concepts that are particularly useful in studying the physical processes associated with freezing soil are

1. Thermodynamic equilibrium requires a balance of thermal, mechanical, and chemical forces. Thermal equilibrium is reached when temperatures are equal, mechanical equilibrium is reached when there is a balance of mechanical forces, and chemical equilibrium is reached when the chemical potentials of all components of the system are equal.

2. The general equation for mechanical equilibrium between two phases—i.e., the interface is curved, rather than planar—is $(P_a - P_b)dV = \Psi dA_r$ (eq 17).

This equation applies to interfaces between all phases of a substance (solid/liquid, vapor/liquid, and solid/vapor interfaces) and is the physical reason for capillary rise of liquids in porous materials.

3. The Gibbs–Duhem equation,

$$\sum_i \eta_i d\mu_i = -SdT + VdP$$

(eq 31), is useful when applied to water in freezing soils.

4. The concept of osmotic pressure is useful in formulating expressions for total soil water pressure. This is because soil water contains solutes; in addition, the influence of soil particle surfaces can be "approximated" as solutes. Expressions for the osmotic potential of a dilute solution are

$$\Pi = \frac{-RT \ln x}{\bar{V}^o}$$

(eq 45) and $\Pi = \tilde{c} RT$ (eq 46).

THERMODYNAMIC TREATMENT OF FROST HEAVE

Early contributions

The first researchers to make significant progress in understanding frost heave were Taber (1929, 1930) and Beskow (1935). Taber (1929, 1930) established with certainty that frost heave does not occur because of the expansion of soil water upon freezing. He proved that pore size influenced the total amount of frost heave for given freezing conditions and that saturated material with very small pores retains unfrozen water at several degrees below freezing. Taber (1929) established that the pressure from frost heaving is due to the direction of ice crystal growth, which is, in turn, controlled by the direction of heat loss. He deduced that slow crystal growth favored frost heave, and introduced the idea that water exists in a state of tension.

Taber (1930) treated freezing soils as open systems. He developed the idea of a gradient in soil moisture tension that causes water above the water table to flow to the freezing front. He also observed that the rate of heave is continuous under constant temperatures applied at the top and bottom of soil specimens even though the ice lenses are separate and distinct from each other.

Taber hypothesized that during the growth of an ice layer, voids underneath it gradually fill with ice, beginning with the larger ones. As the resistance to the flow of water to the ice lens increases (because of the pores filling with ice), a new layer of ice begins to form near the bottom of the zone of the frost penetration. This is the beginning of the idea of a "frozen fringe," a zone at the freezing front where ice has penetrated the pores, contains no ice lenses, and has very low hydraulic conductivity that can limit rate of heave.

Working independently from Taber, Beskow (1935) also contributed several important concepts to the understanding of soil freezing. However, the English translation of Beskow's 1935 report on frost heave is long, difficult to follow, and uses terms that are not well defined. Some clarifications of terms that he used are listed here.* In Beskow's report, soil water is referred to as capillary water, and adsorbed water is called the water under the radius of influence of the particle. The term "capillary pressure" or "positive capillary pressure" means soil moisture tension. Effective stress (a concept that was not yet well-developed) was referred to as "total compressive force," or just "pressure." Two other things are noted: 1) that Beskow described only the "saturated capillary fringe" in all of his discussions that refer to the similarities between soil freezing and

* These terms and their definitions refer only to Beskow's report; they are not necessarily terminology used today. They are provided for the convenience of those who will read his work.

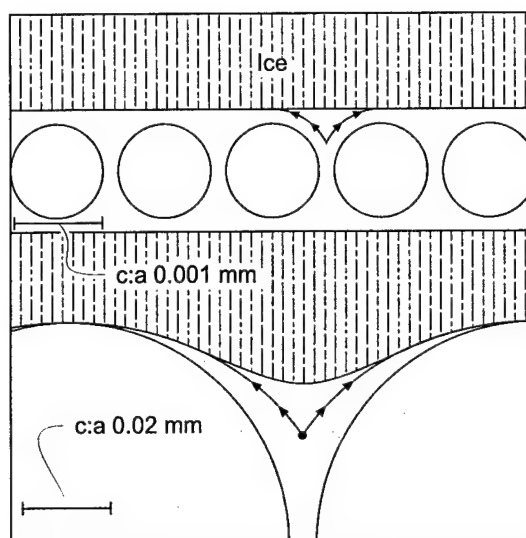


Figure 3. Frost line in two soil types. The upper part of the figure represents a fine-grained frost-heaving soil and the lower part of the figure is a coarse-grained frost-heaving soil (e.g., a coarse silt). The scale of the upper diagram is about 20 times that of the lower diagram. The arrows show the maximum distance that water must travel for frost heave to occur. (After Beskow 1935.)

drying, and 2) that in reference to soil water and soil pressures, Beskow usually (but not always) expressed them in terms of head.

One of the most important ideas contributed by Beskow (1935) is that soil freezing is similar to soil drying—in both cases water changes phase and the amount of liquid water in the soil decreases. Thus, water flow from above the water table to the zone where water is changing into ice is analogous to flow of water to a zone where it is evaporating.

In describing soil freezing, Beskow (1935) noted the freezing point depression of soil water due both to solutes in the water and the "effect of the particle system" (adsorbed water). He constructed freezing temperature curves, showing unfrozen water content vs. temperature and noted that, for saturated fine-grained soils, even the water in the center of the pores is considerably influenced by the particle surface. Ice crystallization is favored farther away from a particle surface and the surface of the ice protrudes down into the pores, with adsorbed water adjacent to it (Fig. 3). Beskow explained that when an adsorbed water film becomes thinner, an increased negative pressure occurs in the unfrozen soil water that induces water to replenish the film.

Beskow (1935) documented the influence of effective stress on frost heave. He said that the total compressive force acting on soil particles during freezing was the sum of the actual load (overburden) pressure

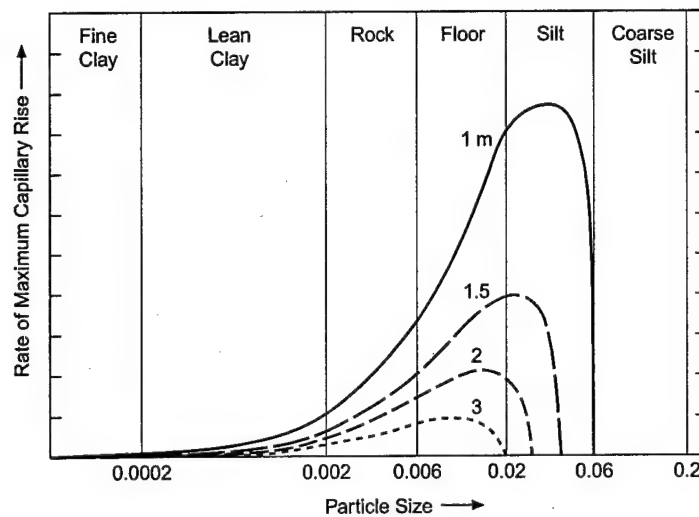


Figure 4. Curves of maximum capillary rise of sorted soils as a function of the average particle diameter for a number of different distances to the groundwater table. (After Beskow 1935.) Note that units of measurement of the rate of capillary rise were not provided.

and the positive capillary pressure (soil moisture tension). In addition, in the tests he performed, equal amounts of overburden pressure and soil moisture tension reduced frost heave rate by the same amount. Beskow (1935) also noticed that when the capillary rise of water in the soil is lower than the distance between the freezing front and the groundwater table, then the soil does not heave.

Beskow froze 32.5-mm-diameter by approximately 40-mm-high insulated specimens from the top down with water available at the base using air temperatures of -2 to -10°C at the top with 0°C water at the base. He believed that his experiments showed that for relatively permeable soils, frost heave rate is fully independent of rate of freezing. However, the temperature variations of his experiments were too small, and the freezing was conducted over too short a time to permit the air temperature variation to produce a noticeable effect on frost heave rate, and we now know that rate of freezing does influence frost heave rate (e.g., Loch 1979).

Beskow (1935) found that, for relatively coarse soils, heave rate drops off rapidly with increasing grain size; however, for fine soils, heave rate drops off slowly with decreasing grain size. The curves are shaped roughly as those shown in Figure 4 (with heave rate being on the y-axis). Figure 4 shows the rate of capillary rise vs. particle size. Beskow determined that soil type and effective stress influenced frost heave. However, his laboratory freezing tests are not described in detail, and may be extreme compared to field conditions of freezing. For example, the temperature gradient induced by -2°C at the top surface of a 40-mm-high specimen with

the bottom held at 0°C ($50^{\circ}\text{C m}^{-1}$) is more than twice the maximum temperature gradient measured near the freezing front by other researchers (e.g., Saarelainen 1992, Vikström 1997).

Everett

D.H. Everett (1961) was one of the first researchers to use the principles of thermodynamic equilibrium to describe the processes associated with the freezing of water in porous media. He wanted to answer why, when pore spaces are completely filled with ice, further growth of ice continues and causes either frost damage (in a porous solid) or frost heave (in soil). He used eq 17 in the form

$$P_s - P_l = \Psi_{sl} \left(\frac{dA_r}{dV} \right) = \Psi_{sl} \tilde{K} \quad (47)$$

where P_s is the pressure of the solid crystal, P_l is the pressure in the surrounding liquid, Ψ_{sl} is the interfacial tension between the solid and the liquid, A_r is the surface area of the phase boundary, V is the volume of the crystal, and \tilde{K} is the mean curvature of the solid/liquid interface. Thus, if the solid phase is at a different pressure than the liquid phase, the interface between the phases is curved. For a pure substance, the equilibrium state is determined only by P_s , P_l , and the temperature.

Everett presented a simple model of two cylinders connected by a capillary tube, each closed by a piston (Fig. 5). Both cylinders are initially filled with water, and temperatures are lowered so that ice nucleates and grows in the top cylinder. As freezing proceeds, the pistons move to accommodate expansion of the system.

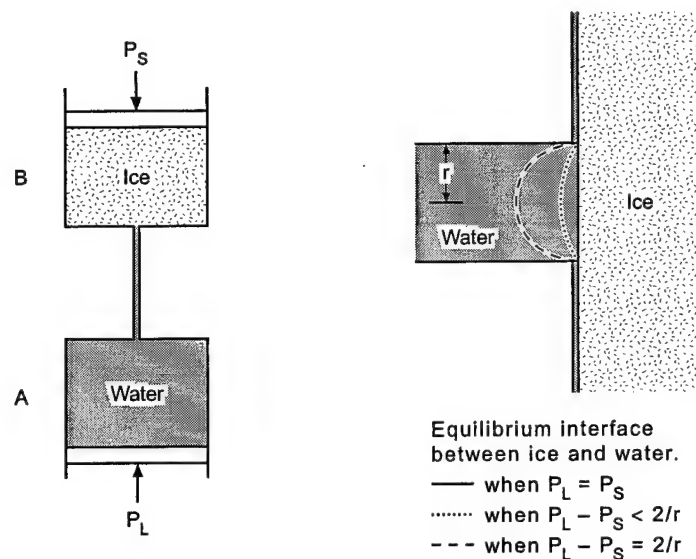


Figure 5. Piston-cylinder model of ice growth. (After Everett 1961.)

Once the top cylinder is ice-filled, further heat loss will result in either 1) upward movement of the upper piston, with flow of water from the bottom cylinder, or 2) propagation of ice along the capillary. If the pressures on the cylinders are equal, $P_s = P_l = P$, then the interface between phases is planar and ice cannot penetrate into the capillary. Ice will form in the top cylinder until all water is removed from the bottom cylinder; i.e., frost heave will occur. An example of this is needle ice* growing at the soil surface. When the needles first begin to grow, there is no overburden and no significant self-weight, thus no chance for P_s to develop.

If the pressure on the ice phase, P_s , can be maintained at a higher level than the liquid, then the chemical potential of the ice in the cylinder (bulk ice) will increase. (For example, as the needle ice at the ground surface grows in length, the weight of the ice exerts a positive ice pressure in the pores at the soil surface.) The freezing temperature becomes depressed and either the ice will melt or heat will be withdrawn until, at the new equilibrium temperature, there is a curved interface between the two phases. If the pressure difference is constant between the ice and the water while further heat is removed, the bulk ice will again grow in the top cylinder as described above. If P_s increases to the point at which the chemical potential of the ice in the piston exceeds that of a hemispherical cap of ice between the ice and water in the pore, then ice growth proceeds down the capillary.

* Everett (1961) referred to the needle-ice as "hoarfrost"; however, hoarfrost refers to the deposition of ice crystals on objects by direct sublimation from water vapor.

Using the equilibrium condition of eq 47 (and noting that a hemispherical cap has the maximum $(\partial A_f / \partial V)$ of various-shaped interfaces), Everett explained that this maximum pressure (with $P_l = 0$) is the maximum heaving pressure that can be reached in porous media. Thus, he concluded that the maximum heaving pressure is a function of pore size and interfacial energy between the ice and water. If this heaving pressure exceeds the overburden pressure in a freezing soil, then frost heave will occur. Here is a basis for understanding why ice can grow against an overburden pressure. Because of the pressure difference across the curved interface, the water can exist at a lower pressure than the ice on the other side of it. For a hemispherical ice front in a pore, $\partial A_f / \partial V = 2/r$; therefore, Everett (1961) concluded that heaving pressure is inversely proportional to the size of the pore radius, r . Note that the pressure difference maintained across an ice/water interface can arise from a reduction of the liquid water pressure as well as from an increase in the bulk ice pressure.

Everett's model considered the mechanical equilibrium between ice and water in porous materials, but ignored the soil particle surface effects on the adsorbed water. As mentioned earlier, a complete thermodynamic equilibrium formulation of the problem would consider thermal, mechanical, and chemical equilibrium. This was the approach taken by R.D. Miller and his students (e.g., Miller et al. 1960, Miller et al. 1975), discussed in the next section.

Miller and Loch

Miller et al. (1960) and Miller et al. (1975) accounted for the osmotic effects related to films adsorbed on soil

particles in the frost heave process by applying the generalized Clapeyron equation (GCE) to the thermodynamic equilibrium between ice and water in soil. In order to clarify that the GCE is based on sound thermodynamics, one of Miller's students, J.P.G. Loch (1978) published a detailed derivation of the GCE. That derivation is now summarized.

Using the Gibbs-Duhem equation (eq 31) for soil ice/water equilibrium, Loch (1978) redefined the chemical potential as the Gibbs free energy per unit mass of a substance so that η_i refers to mass and not moles of a substance, i :

$$\eta_w d\mu_w = -SdT + VdP - \eta_s d\mu_s \quad (48)$$

where the subscripts w and s refer to water and salt, respectively. The equation for the chemical potential for salt in soil water (a form of eq 25) is

$$\mu_s = \mu_s^o(T, P) + \left(\frac{RT}{M_s}\right) \ln x_s \quad (49)$$

where $\mu_s^o(T, P)$ is the chemical potential of the pure salt at the same temperature and pressure as the system, M_s is the molecular weight of the salt, and x_s is the mole fraction of the salt. Making the approximation that

$$x_s \approx \left(\frac{M_w}{M_s}\right) \left(\frac{\eta_s}{\eta_w}\right)$$

we obtain

$$\mu_s = \mu_s^o(T, P) + \left(\frac{RT}{M_s}\right) \ln \left(\frac{M_w}{M_s}\right) + \left(\frac{RT}{M_s}\right) \ln \left(\frac{\eta_s}{\eta_w}\right) \quad (50)$$

Differentiating eq 50 with respect to η_s gives $d\mu_s = (RT/M_s)(1/\eta_s)d\eta_s$, or

$$\eta_s d\mu_s = RTd\left(\frac{\eta_s}{M_s}\right) \quad (51)$$

Substituting eq 51 into eq 48 gives

$$d\mu_w = -\bar{S}dT + \bar{V}dP - \bar{V}RTd\left(\frac{\eta_s}{M_s\eta_w}\right) \quad (52)$$

where \bar{S} and \bar{V} are entropy and volume of solutions per gram of water, respectively. Since the expression in the parentheses of eq 52 is equal to the concentration of the solute in solution, \tilde{c} , eq 52 can be rewritten as

* Loch (1978) apparently redefined the chemical potential in this way in order to arrive at the generalized Clapeyron equation (eq 61) in a form that is convenient to work with because the specific volume of a substance is equal to the inverse of its density.

$$d\mu_w = -SdT + VdP - Vd\Pi \quad (53)$$

since Π , the osmotic pressure, is equal to $RT\tilde{c}$.

If the symbol P_w is used to describe the total soil water potential, then

$$P_w = P - \Pi. \quad (54)$$

Note that P is the pressure of the water excluding osmotic effects and

$$d\mu_w = -\bar{S}dT + \bar{V}dP_w. \quad (55)$$

Equation 55 is integrated after making the substitution that at equilibrium,

$$\bar{S} = \frac{\bar{H}}{T} \quad (56a)$$

to obtain

$$\mu_w = -\bar{H} \ln \left(1 + \frac{\Delta T}{T_o}\right) + \bar{V}P_w$$

or for small ΔT ,

$$\mu_w \approx -\frac{\bar{H}\Delta T}{T_o} + \bar{V}P_w \quad (56b)$$

where \bar{H} is the enthalpy per unit mass of the solution. In eq 56a, T_o is the freezing point of pure water and ΔT is the freezing point depression (K).

Assuming that ice contains no solutes, the chemical potential for pore ice is

$$\mu_i = -\frac{\bar{H}_i\Delta T}{T_o} + \bar{V}_iP + \bar{V}_i\Psi_{iw}\left(\frac{\partial A_r}{\partial V}\right) \quad (57)$$

Setting the chemical potentials of pore ice and water equal (at equilibrium) results in

$$-\left(\frac{\bar{H}}{T_o}\right)\Delta T + \bar{V}P_w = -\frac{\bar{H}_i\Delta T}{T_o} + \bar{V}_iP + \bar{V}_i\Psi_{iw}\left(\frac{\partial A_r}{\partial V}\right) \quad (58)$$

Using the following definitions for the pressure of ice, P_i , and the latent heat of fusion of water per mass,

$$P_i = P + \Psi_{iw}\left(\frac{\partial A_r}{\partial V}\right) \quad (59)$$

$$L_f = \bar{H} - \bar{H}_i \quad (60)$$

and substituting eq 59 and 60 into eq 58 results in the equation of chemical equilibrium between pore ice and water, or the generalized Clapeyron equation:

$$\bar{V}_iP_i - \bar{V}P_w = -L_f\left(\frac{\Delta T}{T_o}\right) \quad (61)$$

Note that the osmotic pressure includes the effects of the diffuse double layer associated with the surface of soil particles (i.e., adsorbed water) through the pressure term, P (eq 54). Equation 61 was referred to later by Miller (1978) as the Clapeyron equation; but it is not the Clapeyron equation one usually finds in Physical Chemistry texts (i.e., eq 38).

Equations 59 and 61 reveal that equilibrium is a function of pore size (through the $\partial A_f/\partial V$ term), hydrostatic pressure of the soil water, osmotic pressure (i.e., presence of solutes and the chemical properties of soil particle surfaces), and temperature. Changes in any of these variables result either in change of location of freezing front or rate of frost heave. For example, if P , P_i , and r are constant throughout a soil body, but there is a spatial distribution of temperature, there will be a gradient in P_w , causing a steady-state flow of water through the system.

This is a more complete formulation of the equilibrium between ice and water in soils than Everett's (1961). This is because the effects of solutes and the chemical properties of soil particle surfaces on the pore water are accounted for through the use of osmotic pressure and the effects of the depressed freezing temperature are also accounted for. Thus, the equilibrium pressure difference that can be sustained between pore ice and pore water, as indicated in eq 61, is much greater than that indicated in eq 47.

Miller

Miller (1978) utilized the concepts described in Loch (1978) and developed a soil freezing model—predicting frost heave as a function of time, temperatures, and pressures. Miller applied concepts developed for treatment of soil drying to model freezing of a saturated, noncolloidal soil. He restricted his modeling efforts to noncolloidal soil, so that the deformations of the soil-ice body are due to the formation of ice lenses, and not compression or expansion of the soil skeleton. This model, called the rigid ice model, includes a rigid, continuous body of ice that comes in contact with continuous pore water in a zone called the frozen fringe (Fig. 6). The frozen fringe is the zone below the deepest ice lens where ice has penetrated the narrowest parts of larger pores between soil particles. This is similar to the capillary fringe where air has penetrated the larger pores in a drying soil. Miller (1978) also defined conditions under which an ice lens will begin to form, and extended beyond development of the thermodynamic equilibrium relations in freezing porous materials (which he utilized) to the transport of mass and heat through unfrozen and partially frozen soil.

Miller used eq 61 in the form

$$\frac{P_i}{\rho_i} - \frac{P_w}{\rho_w} = -L_f \left(\frac{\Delta T}{T_o} \right) \quad (62)$$

where ρ_i and ρ_w are the densities of ice and water, respectively (recall that P_w refers to total soil water potential). He defined a variable, ϕ , as the difference between the ice pressure and the soil water potential divided by the interfacial tension

$$\phi = -\frac{P_i - P_w}{\Psi_{iw}} \quad (63a)$$

or, for air and water

$$\phi_a = -\frac{P_a - P_w}{\Psi_{aw}} \quad (63b)$$

where subscript a refers to air. Equation 63a is an expression for the mean curvature of the ice/water interface in soil pores at equilibrium, and eq 63b applies to the air/water interface. When there are no ice lenses in a frozen soil, pore ice and pore water contents depend on ϕ :

$$\vartheta_w(\phi) + \vartheta_i(\phi) = \eta \quad (64)$$

where ϑ_w refers to volumetric pore water content (note change in notation), ϑ_i to volumetric pore ice content, and η is the total porosity.

Miller noted that the pore pressure, u , has both ice and water components. Thus, he borrowed an expression from Bishop and Blight (1963) for the distribution of pore pressure between the air and water phases and applied it to ice and water:

$$u = \chi(\phi)P_w + [1 - \chi(\phi)]P_i \quad (65)$$

Miller approximates $\chi(\phi)$, known as the stress partition function, as

$$\chi(\phi) \approx \frac{\vartheta_w(\phi)}{\eta} \quad (66)$$

Using similitude between soil freezing and soil drying,

$$\vartheta_w(\phi) = \vartheta_w(\phi_a) \quad (67)$$

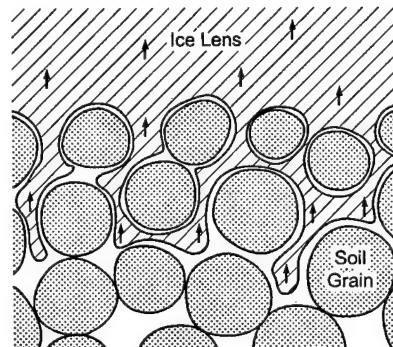


Figure 6. Frozen fringe with ice lens above. (After O'Neill and Miller 1985.)

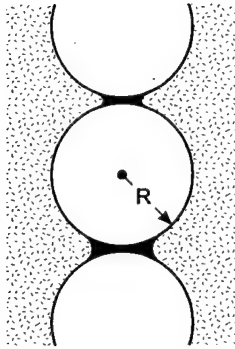


Figure 7. Vertical gradient of pore contents in a vertical column of freezing soil. (After Miller 1978.) Note that the top portion of the soil particle has more film water in contact with ice than the bottom portion and that the curvature of the ice/water interface is greater at the top interface than at the bottom interface.

$$K(\phi) = K(\phi_a) \quad (68)$$

where K is the hydraulic conductivity of the soils (m s^{-1}) and

$$\chi(\phi) = \chi(\phi_a) \quad (69)$$

Using laboratory data for unfrozen water content in a frozen soil, ϑ_w , as a function of temperature, along with all of the relations defined by eq 62 through 69, and Terzaghi's equation for effective stress,

$$\sigma_T = \sigma' + u. \quad (70)$$

Equilibrium values of χ , ϕ , σ' , u , and $K(\phi)$ can be predicted as a function of temperature (or depth) in a freezing soil.

Miller (1978) identified a downward force acting on the granular skeleton in the freezing soil due to a vertical pressure gradient in the adsorbed film. This pressure gradient results from the fact that the top, colder pores have thinner films and therefore greater curvature and greater differences between the ice and water

pressures than the lower, warmer pores (Fig. 7). That is, the pore ice pressure increases upwards from the bottom of the frozen fringe, which causes effective stress to decrease. Figure 8 depicts profiles of soil water pressure, effective stress, and pore pressure in the frozen fringe just prior to ice lens initiation (after Miller 1978). Ice lens initiation occurs when the effective stress reaches 0. At this condition, soil particles become incorporated into upward moving ice. Thus, the ice lens initiation condition is similar to that of Everett (1961). However, the pore pressure that can be generated is greater than that proposed by Everett (1961) due to surface effects of soil particles as well as temperature gradients in the frozen fringe.

Ice movement within a soil is called regelation (refreezing), and it involves the melting, transport around soil grains in adsorbed films, and refreezing of water. The heat released during the change of phase from water to ice in freezing soil is far more significant than the sensible heat transfer. Therefore, Miller ignored sensible heat transfer during freezing, and accounted only for heat transfer due to ice formation:

$$q = -\lambda(\phi) \left(\frac{\partial T}{\partial z} \right) - \rho_i L_f v_i(\phi) \quad (71)$$

where q is the rate of heat flow in the soils, λ is the thermal conductivity of the soil, and v_i is the volumetric ice flux:

$$v_i(\phi) = \vartheta_i(\phi) v_I \quad (72)$$

where v_I is the rate of frost heave. In the unfrozen zone, only heat conduction is considered:

$$q = -\lambda_u \left(\frac{\partial T}{\partial z} \right). \quad (73)$$

Equation 71 contains both heat and mass transfer

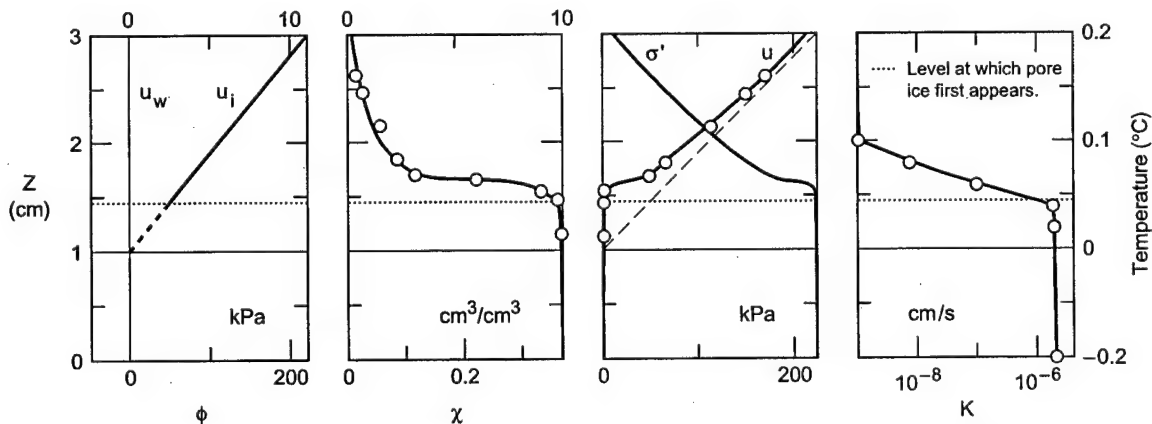


Figure 8. Profiles of soil water pressure, effective stress, and pore pressure in the frozen fringe just prior to ice lens initiation. (After Miller 1978.)

terms, thus coupling models of heat and mass transport in freezing soils. Note that the volumetric ice flux in soil, described by eq 71, consists of the volumetric ice content (a function of ϕ) times the rate of frost heave. The volumetric ice content can change within the frozen fringe because of temperature effects as reflected in the ϕ value.

Frost heave that occurs once a frozen fringe is formed is referred to as secondary heaving, while frost heave with no frozen fringe is primary heaving (assuming an adequate water supply). With primary heaving, only the rate of heat loss controls the rate of frost heave, while with secondary heaving, there is a component of

hydraulic resistivity influencing frost heave rate (Miller 1972).

To complete his model, Miller (1978) applied the conservation of mass and energy in the frozen fringe, along with the relations already mentioned, to obtain the relations among frost penetration rate, rate of frost heave, and rate of heat loss. Miller's rigid ice model was put into finite element form; some results are reported in O'Neill and Miller (1985). Equations of the model were solved for one-dimensional freezing of an initially unfrozen, saturated soil column. A 153-mm soil column of silt with a given function of unsaturated hydraulic conductivity vs. liquid water content was

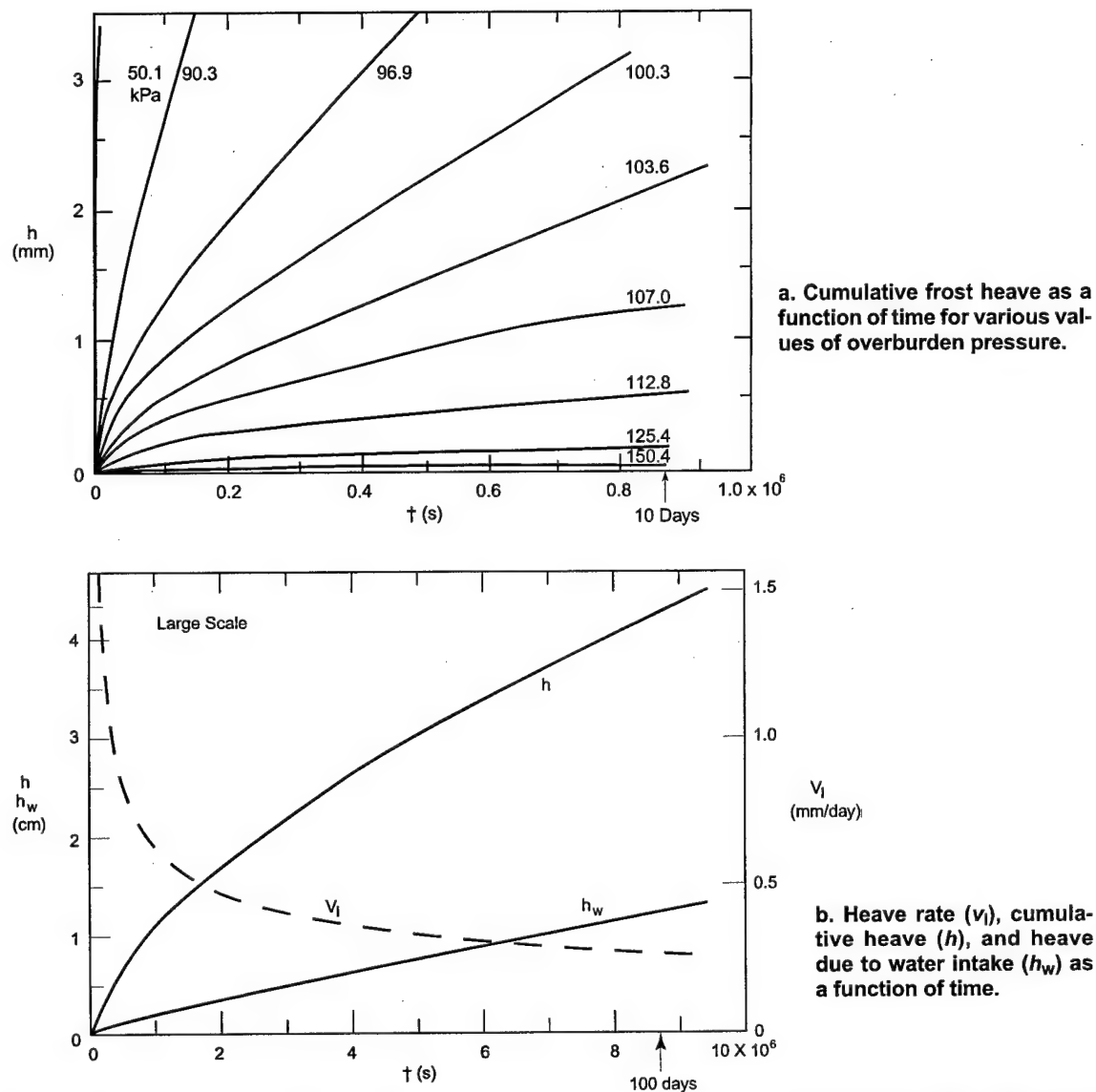


Figure 9. Typical results of Miller's rigid ice model of frost heave, reported by O'Neill and Miller (1985), for a saturated silty soil.

modeled. The specimen was initially at 1°C, then the top temperature was gradually ramped down to -0.5°C. The thermal conductivity of the specimen was computed as a geometric mean of the thermal conductivities of soil solids, ice, and water during freezing. Figures 9a and b show typical results. The model predicts behavior of the soil column during freezing and the values are reasonable.

Black and Miller (1985) applied a simplified version of the rigid ice model to laboratory test results on a silt. They assumed that the liquid water content and the unsaturated hydraulic conductivities were simple Brooks-and-Corey-type exponential functions of ϕ (e.g., Brooks and Corey 1964). Heave and frost penetration rates and temperature gradients in the unfrozen soil were input variables, while temperature gradients in the frozen soil and heaving pressure were outputs. The model accurately predicted temperature gradients, but predicted heaving pressures to be about half of those measured, indicating problems with the experimental procedure that were later found to exist.* The rigid ice model is now available in the form of a MathCad 5.0+ computer program (Black 1995).

The rigid ice model has now been developed into an engineering tool for prediction of heaving due to one-dimensional heat loss. Using the rigid ice model as a basis, Sheng (1994) developed a numerical model of frost heave. This model, called PC-Heave, predicts heave for stratified soils and unsaturated layers. Input variables for PC-Heave are the number of soil layers and their thicknesses, the dry densities, water contents, thermal and hydraulic conductivities and percentage saturation of the soil layers, the boundary temperatures at the top and the bottom, the depth of the groundwater table, and one unfrozen water content at a subfreezing temperature per FSL (a calibration factor). The model predicts heave, location of ice lenses, frost penetration, segregation temperature, and suction in the pore water of the frozen fringe with time.

The modeling equations are the mass and heat balances at the base of the warmest ice lens and for the frozen fringe, Darcy's Law, and the expression for the pore water pressure in the frozen fringe that incorporates the generalized Clapeyron equation (Sheng 1994). The model has been verified using both field and laboratory soil freezing information.

Gilpin

Gilpin (1979, 1980) developed a model very similar to the rigid ice model. He assumed that the chemical potential of the water in the adsorbed film is lowered

by the surface effects of the solid:

$$\mu_L = \mu_{LB} - \mu_L \Psi \quad (74)$$

where μ_L is the chemical potential of the liquid in the film, μ_{LB} is the chemical potential of the bulk liquid, and $\mu_L \Psi$ is the depression in the chemical potential from bulk water caused by the presence of the solid surface. Gilpin assumed that it had the form of a power law relationship:

$$\mu_L \Psi = ay^{-\alpha} \quad (75)$$

where y is the distance from the soil particle surface and a and $-\alpha$ could be adjusted as needed.

The chemical potential of the bulk water is given by (an integrated form of eq 19)

$$\mu_{LB} = \mu_{L0} + \bar{V}_L(P_L - P_0) - \bar{S}_L(T_L - T_0) \quad (76)$$

where μ_{L0} is the chemical potential at a reference condition, (P_0 , T_0). Substituting eq 75 into eq 74 and 74 into 76 at equilibrium (i.e., $\mu_L = \mu_{L0}$) and assuming that the temperatures of the bulk and film water are equal leads to the following expression for the variation of pressure in film water, with a distance from the solid surface (Fig. 10):

$$(P_L - P_0) = \left(\frac{a}{\bar{V}_L} \right) y^{-\alpha} \quad (77)$$

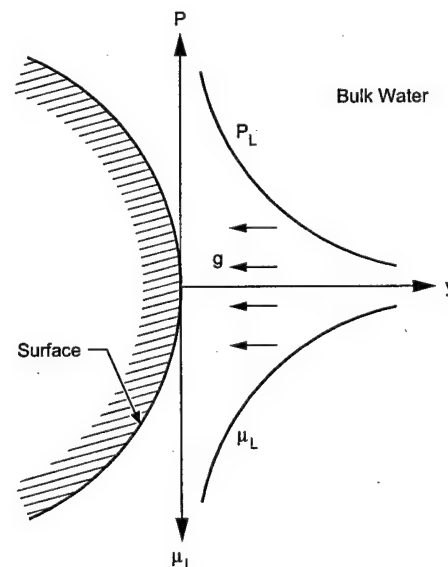


Figure 10. Gradient in film water pressure next to a soil particle as described by Gilpin (1980); note similarity to ion distribution according to the diffuse double layer theory.

* Personal communication, Dr. Patrick Black, CRREL, Hanover, New Hampshire, 1999.

Static equilibrium in the film perpendicular to the particle surface requires that the particle must exert a body force per unit volume, g , equal to

$$g = \frac{\partial(P_L - P_0)}{\partial y} \quad (78)$$

If the film is not of a uniform thickness, the body force will drive tangential fluid flow to return the film to a uniform thickness. Using equilibrium thermodynamics, Gilpin (1979) then derived the following expression for the thickness of the film (h) as a function of temperature, pressure, and surface curvature:

$$(\bar{V}_s - \bar{V}_L)P_{Lh} + \bar{V}_s\Psi_{SL}\tilde{K} - L_f\frac{T_L - T_0}{T} = ah^{-\alpha} \quad (79)$$

where P_{Lh} is the difference between the pressure in the film at the ice/water interface and the reference pressure. Using this model along with experimental results, Gilpin (1979) concluded that the value of α is approximately 2.

Gilpin (1980) used an approach similar to Miller's in developing a model to predict frost heave in soils, although his model was simpler due to his initial approximations. His model includes the model of the pressure gradient in the water near a solid/liquid interface described above. This is similar to the use of osmotic pressure as described by Loch (1978). Gilpin's model is also based on the GCE:

$$\bar{V}_sP_{Lh} - \bar{V}_s\Psi_{SL}\tilde{K} = \frac{L_f\Delta T}{\bar{V}_sT} \quad (80)$$

Assuming that Darcy's law is valid, Gilpin derived the relationship between driving potential tangential to soil particle surfaces and flow rate of water in the continuous liquid phase. The equation that resulted is

$$v_w = -K\left(\frac{\bar{V}_s}{g}\right)\frac{\partial}{\partial z}\left(P_s + \frac{L_f\Delta T}{\bar{V}_sT}\right) \quad (81)$$

where P_s is the pressure of the ice phase. Thus (like the rigid ice model) the flow rate is governed by the ice pressure gradient, temperature gradient, and hydraulic conductivity in the frozen fringe. Gilpin assumed that the pore ice formed a continuous three-dimensional network, but that it remained stationary. To address the question of ice lens formation, he used relations among interface curvature, pressure, and temperature to estimate the ice pressure at which the force of contact between two particles will drop to zero. For most situations of interest, this ice pressure is equal to the overburden pressure, P_{OB} , plus the pressure difference across the ice/water interface:

$$P_{SEP} = P_{OB} + \left(\frac{2\Psi_{sl}}{R}\right) \quad (82)$$

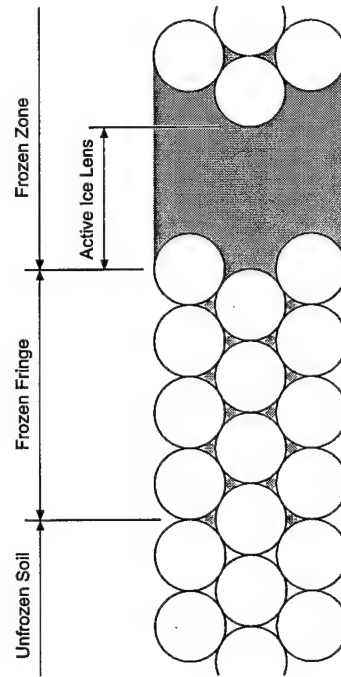


Figure 11. Gilpin's idealized model of the frozen fringe in a matrix of uniform spheres. (After Gilpin 1980.)

He estimated the hydraulic conductivity of the frozen fringe based on simplifying assumptions regarding the packing of uniform spheres (Gilpin 1980). Figure 11 is Gilpin's idealized model of a frozen fringe in a matrix of uniform spheres, showing a graph of the temperature and pressure gradients.

Gilpin (1980) developed numerical solutions to his mathematical model of frost heave for a 100-mm column. The "soil" was a matrix of 2- μ m uniform spheres. A constant subfreezing temperature was imposed on the top surface, and a temperature slightly above freezing was imposed on the bottom surface. Gilpin's results are qualitatively and quantitatively similar to those reported in O'Neill and Miller (1985).

Summary of the thermodynamic formulations of frost heave

Taber (1929) proved that frost heave was not caused by the volume expansion of water upon freezing, and introduced the idea that frost heave was dependent on freezing rate and occurred in a direction perpendicular to heat flow. Beskow (1935) contributed the important idea that frost heave is analogous to soil drying and that in fine-grained soils frost heave is sometimes limited by water flow in the soils. He also noted that in-

creasing effective stress (by some combination of lowering the water table and increasing the overburden pressure) reduces the rate of frost heave of a soil, all other things being equal (Beskow 1935). Beskow incorrectly concluded that frost heave rate in saturated soils was independent of freezing rate, and his generalizations about frost heave were for a constant rate of freezing.

Everett (1961) applied equilibrium concepts to explain frost heave. He considered the mechanical equilibrium between pore ice and pore water, thereby concluding that the maximum pressure difference in a heaving soil is determined by the smallest pore sizes. This was an important theoretical advancement; it provided a qualitative explanation for what is now known as primary frost heaving. However, he did not consider temperature and chemical effects that can result in even smaller radii of curvature between ice and water in soil pores (leading to greater ice-water pressure differences).

Miller et al. (1960), Miller et al. (1975), and Loch (1978) developed a more complete thermodynamic equilibrium of pore ice and water; thus, chemical and thermal equilibrium are included. The Generalized Clapeyron Equation, based on the equilibrium of ice and water in soils is utilized by the thermodynamically based models of Miller (1978) and Gilpin (1980).

Miller (1978) and Gilpin (1980) used the equilibrium relationships as described by Loch (1978) and added heat and mass transfer in the frozen fringe to model frost heave. Darcy's Law and Fourier's Law describe heat and mass transfer in the frozen fringe, respectively, and mass flow and heat flow are coupled by one equation that describes heat transfer in the frozen soil. Ice lenses start to grow when the effective stress in the frozen fringe becomes zero (Miller 1978, Gilpin 1980). The rigid ice model assumes that ice is one continuous rigid body that grows by regelation (Miller 1978). Gilpin's model also assumes that the ice forms a continuous three-dimensional network, but it remains stationary in the frozen fringe. The main difference between the models is that Gilpin made a few reasonable simplifying assumptions that allowed the model to be programmed rather easily. However, more recent work with the rigid ice model has made it relatively easy to use (e.g., Black 1995). Both models predict the same qualitative frost heave behavior, and are similar quantitatively. The rigid ice model is also the basis for the more recently developed numerical model used to predict frost heave in the field, known as PC heave (Sheng 1994).

SUMMARY OF CURRENT UNDERSTANDING OF FROST HEAVE

In the introduction of this report the idea that the frost heave of soils can be understood from the stand-

point of thermodynamics was introduced. Thermodynamic fundamentals and thermodynamic equilibrium conditions are presented in the sections "Thermodynamic fundamentals" and "Thermodynamic equilibrium," respectively. In "Thermodynamic treatment of frost heave," the modeling of frost heave based on equilibrium thermodynamics was briefly presented. In this section, a brief summary of the current understanding of frost heave, based on the work reviewed above, is presented without reference to any equations. This is intended to help readers better understand frost heaving. It makes use of similarities between freezing and drying since most readers are more comfortable thinking about the evaporation of water from soils than about frost heave.

Drying is due to evaporation, or the conversion of water to vapor by the addition of heat, whereas freezing is the conversion of liquid to solid by the removal of heat. Conditions required for evaporation of water from soil include 1) a supply of heat, 2) a means of transporting the vapor away from the pores, and 3) a supply of water. Conditions required for frost heave include 1) a removal of heat, 2) a means of transporting the ice away from the pores (i.e., the ice lenses), and 3) a supply of water. (Note, however, that the effective stress must become zero in order for an ice lens to initiate—this is discussed in detail later.)

It may also be helpful to keep in mind the differences between the capillary fringe and the frozen fringe. The capillary fringe is the soil just above the water table where water rises up through capillary action. This layer ranges in thickness from zero to a meter or so, and it depends on the pore sizes of the materials. In a soil that frost heaves, recall that the frozen fringe is the soil just below the bottommost ice lens and above the unfrozen soil where water and ice coexist in soil pores.

Consider evaporation from soils. If the water in the pores of the capillary fringe is in equilibrium with the water vapor across curved liquid/vapor interfaces there is no movement or phase change of water (i.e., no net evaporation). If water vapor is removed from the pores by convection, for example, liquid water will change phase to replace the vapor and water will flow up through the soil pores to replenish the liquid water. If the rate of water loss due to phase change is matched by the rate of water flow to replenish the liquid water, no change in the water distribution of the capillary fringe occurs. If the soil at the location of phase change cannot replenish the water for the given rate of heat addition, (e.g., due to low hydraulic conductivity), the capillary fringe will increase in depth and/or thickness.

Frost heave occurs by a process very similar to soil freezing. In freezing soils, pore water is in equilibrium with ice across curved liquid/solid interfaces. However,

unlike the liquid/vapor interface in soil pore, the liquid/ice interface is such that the ice can exert a positive pressure on the soil skeleton. When the pore pressures in a freezing soil reach the soil strength at that location (i.e., the effective stress becomes zero), an ice lens initiates. Once an ice lens is established, liquid water is removed from the pores because of the phase change and water flows up through the soil to replenish the liquid water. The water flows through unfrozen soil and through the frozen fringe to reach the ice lens. If the rate of water loss due to phase change is matched by the rate of water flow to replenish the liquid water, no change in the water distribution of the frozen fringe occurs and the ice lens will continue to grow in thickness. If the hydraulic conductivity of the soil limits the rate of water replenishment to the ice lens for the given rate of heat loss, soil water will freeze at increasing depths with associated changes in the depth and thickness of the frozen fringe. In addition, if there is a location in the frozen fringe at which the effective stress reaches zero, a new ice lens will begin to develop. The new ice lens will grow at a faster rate than the one above it because the hydraulic conductivity of soil immediately below is greater, although the ice lenses above the new one may continue to grow.

The frozen fringe thickness depends on the temperature gradient, overburden pressure, and the specific soil. High overburden pressure and low temperature gradients increase the thickness of the frozen fringe. The ice is a continuous body from the frozen fringe up through the ice lens, and it moves by regelation, or continuous ice-water phase change, accompanied by locally circulating liquid flow.

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removed from the adjacent pores because of phase change, and water flows up through the soil to replenish the liquid water. If the rate of water loss caused by phase change is matched by the rate of water flow to replenish the liquid water, the ice lens will continue to grow in thickness. If the hydraulic conductivity of the soil limits the rate of water replenishment to the ice lens for the given rate of heat loss, soil water will freeze at increasing depths with associated changes in the depth and thickness of the frozen fringe.